# Thermal intramolecular Diels–Alder reaction of furan; synthesis of nitrogen tetracycles, isobenzofuran and isobenzothiophene

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Thermal intramolecular Diels–Alder (IMDA) reaction of furan cored compounds has been further investigated; a series of key precursors to the IMDA reaction of furan diene (**9a–c**) have been prepared *via* facile alkylation and protection. While the cycloaddition process for (**10a–c**) was afforded in hot toluene, a commercial microwave (2450 MHz) was used for the synthesis of (**12a–b**). Treatment of fused oxy- and thio-heterotricycles (**12a–b**) with borontrifluoride-etherate in dichloromethane at –78°C cleaved epoxy bridge and concomitant aromatisation gave the isobenzo-furan and thiophene (**13a–b**) in 72–76% yields respectively.

**Keywords:** intramolecular Diels–Alder, cycloaddition, aromatisation.

## Introduction

Diels–Alder reactions involving furan as a diene form oxanobornenes that have been used in the synthesis of numerous complex targets and as an intermediate in the synthesis of natural products such as carbohydrates and prostaglandins.[1] However, the facile retro-Diels–Alder reaction and the low reactivity of furan as a diene as a result of its aromatic character make the Diels–Alder reaction of furan one of the most difficult cycloaddition.[2] We have been studying intramolecular free radical reaction of furan with carbon chain tether,[3] and recently reported that the under thermal condition the bromofurfurylalkenes, (**1**) with heteroatom possessed tether undergoes intramolecular cycloaddition and gives heterofused tricycles (**2**) (32–44% overall) as shown in Fig. 1.[4]

Having seen recent papers[5] on IMDA reactions, we now report our additional findings regarding synthesis of fused tetracycles and substituted aromatic structures. One can utilise these compounds as a powerful strategy at the intermediate stages in a total synthesis, and develop the furan chemistry.

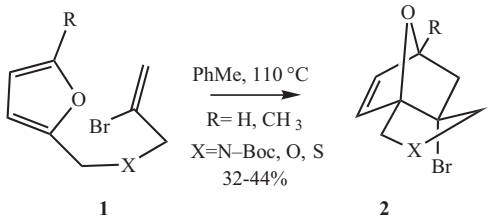


**Fig. 1**

## Results and discussion

Fused tetracyclic bromides, (**10a–c**) were prepared by a procedure shown in Fig. 2. Bromination[6] of the commercially available cyclopentenone, (**3**) by employing molecular bromine and triethylamine was followed by selective Luche's reduction of 2-bromocyclopentenone. Reaction of resulting alcohol with phosphorous tribromide and pyridine gave 2,3-dibromocyclopentene, (**4**) ($n$ = 1) in high yields.[7] Known 2,3-dibromocyclohexene (**4**) ($n$ = 2) was derived from cyclopentene, (**6**) by a step economy; addition of dibromocarbene to cyclopentene, followed by thermal ring expansion gave the corresponding 2,3-dibromocyclohexene, (**4**) ($n$ = 2) in 78% yield.[8] Displacement of allylic bromide in **4** (n = 1, 2) generated (**8a–c**) in 90–93% yields, which were then converted to their carbamates, (**9a–c**) under standard condition.[9]

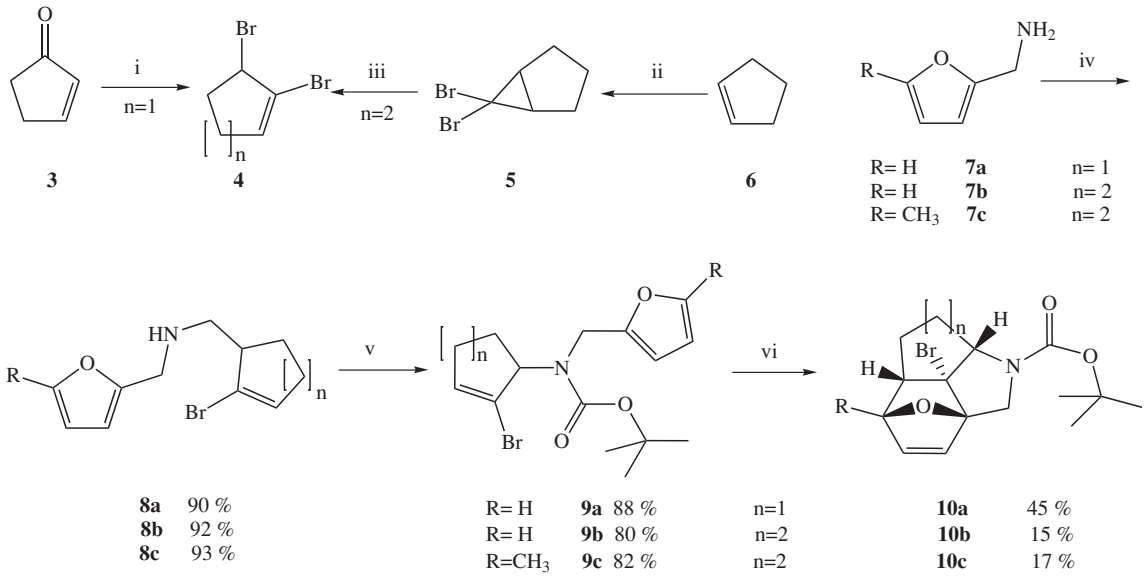


**Fig. 2** (i) $Br_2$, $Et_3N$, DCM, 0°C, 98%; $NaBH_4$, $CeCl_3.7H_2O$, MeOH, 0°C, 97%; $PBr_3$, pyridine, PhH, 0°C→ reflux, 68%; (ii) KO$^t$Bu, $CHBr_3$, pentane, 0°C; (iii) heat 155°C, 1 h, 78%; (iv) 2,3-dibromocyclopentene or 2,3-dibromocyclohexene (4), $K_2CO_3$, THF, reflux, 3 d; (v) $(BOC)_2O$, DMAP, DCM, 0°C, 2 h; (vi) heat, PhMe, 4 days.

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Non-protected bromoalkenylfuran compounds (**8a–c**) do not proceed cycloaddition even under forced condition. Therefore, *tert*-butoxy, as a bulky protecting group, was used as a steric buttress[10] on nitrogen to encourage the cycloaddition process. The *N*-alkylated derivatives (**9a–c**) were heated as solution in toluene at temperatures between 95 and 110°C. Of these derivatives the carbamate (**9a**), showed greatest degree of intra-molecular cycloaddition; at 110°C, 45% of the cycloadduct (**10a**) formed, the remainder being uncyclised starting material. According to the our previous X-ray crystallographic report[11] on (**9b**) as an example; the molecules are linked only by weak van der Waals interactions and it is found that the bromo attached cyclohexane ring adopts a half-chair conformation with torsion angle as given. The Br–C bond distance [1.939(9) Å] is not significantly different from the value reported for a pure Br–C single bond (1.94 Å).[12] Presumably, the position of dien-dienophile to each other is the main reason of modest yields.

However, this facile thermal closure gives an unusual tetracycles, possessed a quaternary carbon with a bromine atom. Additionally, the process could also be an initiation step to the some problematic intermediate of synthetic projects, like in which, even nitrogen tricycle opens and gives acyclic product as soon as the adjacent carbonyl group has been reduced.[13]

In order to utilise our chemistry, we also achieved the cycloaddition process in a commercial microwave under solvent free condition. It is found that, 12 min irradiation for (**11a–b**)[3b] gives the best result, further irradiation decomposes the furans. Although, the yields was slightly lower than the thermal process, the considerable time saving make this procedure as an alternative application (Fig. 3).[14,15]

Treatment of (**12a–b**) with borontrifluorate-etherate in dichloromethane at –78°C afforded the isobenzo-furanol and thiophenol moieties, (**13a–b**) in 76% and 72% yields. A mechanistic rationale for the formation of (**13a–b**) is also outlined in Fig. 4. The mechanism presumably involves the Lewis Acid ($BF_3.Et_2O$) catalysed ring opening of (**12a–b**) to form allylic cation (**14a–b**) which upon proton exchange and decomplexation affords the enol (**15a–b**), which undergoes hydrogen bromide elimination to fused aromatic derivatives (**13a–b**).

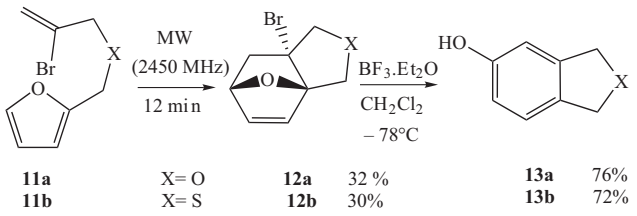


**Fig. 3**

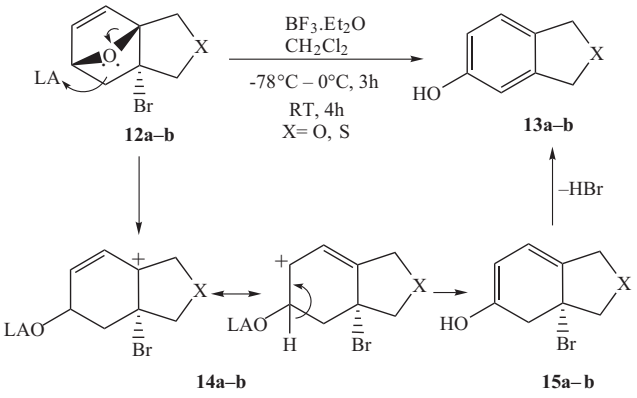


**Fig. 4**

Once again, thermal IMDAF reaction could be used as a key step as an entrance to more complex fused ring systems in combinatorial organic chemistry. Additionally, intramolecular Diels–Alder cycloadditon process of furans is achievable in a microwave under solvent free condition. Utility of thermal IMDAF reaction was shown by transforming heteroaromatic compounds to the bicycle-benzoaromatic compounds. Further progress has been carrying out about to cleavage of oxa-bridge by using different Lewis acids and will be reported in due course.

## Experimental

Solvents and reagents were freshly distilled as follows: tetrahydrofuran (THF) and diethyl ether (E) were distilled from sodium/benzophenone; dichloromethane (DCM) and toluene were distilled from calcium hydride. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica plates (Macharey Nagel sil G $UV_{254}$). Compounds were visualised using UV fluorescence, alkaline potassium permanganate solution or acidic cerium (IV) sulfate solution. Column chromatography was carried out Macharey Nagel Kieselgel 60 (230–240 mesh). $^1H$ NMR spectra were recorded on a Bruker 300 MHz DPX 300 spectrometer. The chemical shifts are quoted in ppm, as δ values downfield of tetramethylsilane (TMS) or relative to the residual solvent resonance. IR spectra were recorded on a Perkin-Elmer 1720 spectrophotometer; solid samples were recorded using potassium bromide discs, and liquid samples were recorded as thin films. Elemental analysis (EA) were carried out by the microanalytisches laborataorium des institüts für Organische und Biomoleculare Chemie der Universitat Gottingen, electron ionisation mass spectra (EI, 70eV) were obtained on a Fisions VG Autospec mass spectrometer.

*Synthesis of furanyl amines* (**8a–c**)

To a stirred solution of furfurylamine (**7a–c**) (**7a,b** supplied from Fluka, Cat. No: 48120**, 7c** supplied from Aldrich, Cat. No: 415626) (11.66 mmol) in THF (40 ml) was added 2,3-dibromocyclopentene or 2,3-dibromocyclohexene (5.83 mmol) and the resulting solution was heated to reflux for 12 h. A portion of potassium carbonate (3.70 g, 26.02 mmol) was then added, and the reaction mixture was heated at reflux for a further 48 h. On cooling, a precipitate was formed which was washed with diethyl ether (3 × 25 ml). The filtrate was extracted with 10% NaOH (40 ml) and the combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford following compounds;

*2-Bromo-N-(furan-2-ylmethyl)cyclopent-2-en-1-amine* (**8a**): Colourless oil, (1.27 g, 90%). TLC, (hexane: EtOAc (7:3)), $R_f$: 0.32; $\upsilon_{max}$ (thin film)/$cm^{-1}$: 3323 (w, N–H), 2924 (s, C–H), 2851 (w, C–H), 1153 (s, C–O), 607 (w, C–Br); $\delta_H$ (300 MHz, $CDCl_3$): 7.30(d, 1H, $J$ = 1.8 Hz), 6.25 (dd, 1H, $J_1$ = 1.8 Hz, $J_2$ = 3.1 Hz, AB), 6.20 (d, 1H, $J$ = 3.1 Hz, AB), 5.98 (dd, 1H, $J_1$ = 2.3 Hz, $J_2$ = 3.8 Hz), 3.83–3.70 (m, 3H), 3.45 (brs, NH), 2.39–1.78 (m, 4H); $\delta_C$ (75.5 MHz, $CDCl_3$): 152.7 (*q*), 142.1, 134.2, 123.3 (*q*), 110.3, 107.6, 65.9, 42.3, 30.8, 28.8; *m/z*: 244 [$M^+$ + H ($^{81}$Br), 38%], 242 [$M^+$ + H ($^{79}$Br), 38%], 162 [$M^+$ ($^{81}$Br)–($^{81}$Br), 1.4%], 147 [$(C_5H_6{}^{81}Br)^+$, 15%], 81 [$(C_5H_5O)^+$; 100%], EA. ($C_{10}H_{12}BrNO$): Calculated (Found)%: 49.61 (49.57)% C, 5.00 (5.16)% H, 5.79 (5.85)% N.

*2-Bromo-N-(furan-2-ylmethyl)cyclohex-2-en-1-amine* (**8b**): Colourless oil, (1.38 g, 92%). TLC, (hexane: EtOAc (8:2)), $R_f$: 0.52; $\upsilon_{max}$ (thin film)/$cm^{-1}$: 3330 (w, N–H), 2933 (s, C–H), 2859 (w, C–H), 1170 (s, C–O), 600 (w, C–Br); $\delta_H$ (300 MHz, $CDCl_3$): 7.37 (d, 1H, $J$ = 2.0 Hz), 6.31 (dd, 1H, $J_1$ = 2.0 Hz, $J_2$ = 3.1 Hz, AB), 6.22 (d, 1H, $J$ = 3.1 Hz, AB), 6.19–6.16 (m, 1H), 3.88 (d, 1H, $J$ = 12.4 Hz, AB), 3.77 (d, 1H, $J$ = 12.4 Hz, AB), 3.32–3.30 (m, 1H), 2.11–1.57 (m, 6H), 1.26 (brs, NH); $\delta_C$ (75.5 MHz, $CDCl_3$): 155.7 (q), 143.8, 134.6, 127.8 (q), 112.1, 109.0, 59.7, 45.4, 31.2, 29.9, 20.1; *m/z*: 258 [$M^+$ + H ($^{81}$Br), 36%], 256 [$M^+$ + H ($^{79}$Br), 36%], 190 [$M^+$($^{81}$Br)–($C_4H_3O$), 6%], 176 [$M^+$($^{81}$Br)–($C_5H_5O$), 20%], 174 [$M^+$($^{79}$Br)–($C_5H_5O$), 20%] 96 [$(C_5H_6ON)^+$, 20%], 81 [$(C_5H_5O)^+$; 100%]; EA.($C_{11}H_{14}BrNO$): Calculated (Found)%: 51.58 (51.60)% C, 5.51 (5.48)% H, 5.47 (5.47)% N.

*2-bromo-N-((5-methylfuran-2-yl)methyl)cyclohex-2-en-1-amine* (**8c**): Colourless oil, (1.46 g, 93%). TLC, (hexane: EtOAc (8:2)),

$R_f$ 0.50; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 3316 (w, N–H), 2927 (s, C–H), 2860 (w, C–H), 1180 (s, C–O), 600 (w, C–Br); $\delta_H$ (300 MHz, $CDCl_3$): 6.12 (s, 1H), 6.02 (s, 1H), 5.80 (s, 1H), 3.75 (d, 1H, *J* = 12.2 Hz, AB), 3.65 (d, 1H, *J* = 12.2 Hz, AB), 3.27 (s, 1H), 2.20 (s, 3H), 2.05–1.67 (m, 6H), 1.53 (brs, NH); $\delta_C$ (75.5 MHz, $CDCl_3$): 151.7 (q), 151.5 (q), 132.6, 125.9 (q), 107.9, 105.9, 57.6, 43.5, 29.2, 27.9, 18.2, 13.6; *m/z*: 271 [M$^+$($^{81}$Br), 11%], 269 [M$^+$($^{79}$Br), 11%], 190 [M$^+$($^{81}$Br)–($^{81}$Br), 4%], 110 [ ($C_6H_8ON$) 19%], 95 [ ($C_6H_7O$) 100%]; EA.($C_{12}H_{16}BrNO$), Calculated (Found)%: 53.35 (53.51)% C, 5.97 (6.02)% H, 5.18 (5.10)% N.

*Synthesis of furfuryl carbamides* (**9a–c**)

To a stirred solution of amine (**8a–c**) (5.35 mmol) and di-tert-butoxy dicarbonate $(BOC)_2O$ (1.17 g, 5.35 mmol) in DCM (10 ml) was added *N,N*-dimethylaminopyridine (0.07 g, 0.54 mmol) at 0°C. The reaction mixture was stirred for 2 hours at ambient temperature and then concentrated under vacuum. The residue was subjected to flash column chromatography to afford the precursors;

*tert-Butyl 2-bromocyclopent-2-en-1-yl-(2-furylmethyl)carbamate* (**9a**): Colourless oil, (1.61 g, 88%). TLC, (hexane: EtOAc (7: 3)): $R_f$ 0.73; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 2977 (s, C–H), 2929 (s, C–H), 1702 (s, C=O), 1169 (s, C–O), 603 (m, C–Br). $\delta_H$ (300 MHz, $CDCl_3$): 7.28 (d, 1H, *J* = 1.8 Hz), 6.28 (dd, 1H, $J_1$ = 1.8 Hz, $J_2$ = 3.0 Hz), 6.13–5.97 (m, 2H), 4.57–4.41 (m, 1H), 4.30 (d, 1H, *J* = 12.0 Hz), 3.95 (d, 1H, *J* = 12.0 Hz), 2.30–1.92 (m, 4H), 1.40 (s, 9H); $\delta_C$(75.5 MHz, $CDCl_3$): 155.5 (q), 152.3 (q), 141.4, 135.0, 122.0 (q), 110.3, 106.9, 80.2 (q), 65.0, 40.1, 30.7, 28.3 (3 × C), 27.0; *m/z* (GC–MS): 343 [M$^+$($^{81}$Br), 5%], 341 [M$^+$($^{79}$Br), 5%], 286 [M$^+$($^{81}$Br)–($^t$Bu), 20%], 284 [M$^+$($^{79}$Br)–($^t$Bu), 21%], 205 [M$^+$($^{81}$Br)–($^t$Bu + $^{81}$Br), 35%], 139 [M$^+$($^{81}$Br)–($^t$Bu + $C_5H_6{}^{81}$Br), 75%], 81, 57; EA. ($C_{15}H_{20}BrNO_3$), Calculated (Found)%: 52.64 (53.44)% C; 5.89 (5.96)% H, 4.09 (3.62)% N.

*tert-Butyl 2-bromocyclohex-2-en-1-yl-(2-furylmethyl)carbamate* (**9b**): Colourless crystals, (1.52 g, 80%); m.p. 69–71°C; TLC, (Hexane: EtOAc (4:1)): $R_f$ 0.75; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 2975 (s, C–H), 2933 (s, C–H), 1702 (s, C=O), 1164 (s, C–O), 607 (m, C–Br). $\delta_H$ (300 MHz, $CDCl_3$): 7.32 (d, 1H, *J* = 1.9 Hz), 6.34–6.30 (m, 1H), 6.24 (dd, 1H, $J_1$ = 1.9 Hz, $J_2$ = 3.1 Hz, AB), 6.14 (d, 1H, *J* = 3.1 Hz, AB), 4.92–4.90 (m, 1H), 4.51 (d, 1H, *J* = 12.4 Hz, AB), 3.92 (d, 1H, *J* = 12.4 Hz, AB), 2.13–1.58 (m, 6H), 1.43 (s, 9H); $\delta_C$ (75.5 MHz, $CDCl_3$): 155.3 (q), 153.7 (q), 143.4, 133.5, 127.3 (q), 113.4, 109.1, 82.2 (q), 58.0, 45.1, 29.7, 29.0 (3 × C), 28.4, 21.5; *m/z*: 357 [M$^+$($^{81}$Br), 10%], 355 [M$^+$($^{79}$Br), 10%], 300 [M$^+$($^{81}$Br)–($^t$Bu), 15%], 298 [M$^+$($^{79}$Br)–($^t$Bu), 15%], 256 [M$^+$($^{81}$Br)–(Boc), 100%], 254 [M$^+$($^{79}$Br)–(Boc), 100%], 161, 81, 57; EA.($C_{16}H_{22}BrNO_3$), Calculated (Found)%: 53.94 (53.61)% C, 6.22 (6.51)% H, 3.93 (3.70)% N.

*tert-Butyl 2-bromocyclohex-2-en-1-yl[(5-methylfuran-2-yl)methyl] carbamate* (**9c**): Colourless crystals, (1.63 g, 82%); m.p. 65–67°C; TLC, (hexane: EtOAc (4:1)): $R_f$ 0.72; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 2986 (s, C–H), 2945 (s, C–H), 1716 (s, C=O), 1164 (s, C–O), 610 (m, C–Br). $\delta_H$ (300 MHz, $CDCl_3$): 6.35–6.32 (m, 1H), 6.00 (d, 1H, *J* = 3.0 Hz, AB), 5,88 (d, 1H, *J* = 3.0 Hz, AB), 4.70–4.90 (m, 1H), 4.45 (d, 1H, *J* = 12.1 Hz, AB), 3.80 (d, 1H, *J* = 12.1 Hz, AB), 2.26 (s, 3H), 2.11–1.55 (m, 6H), 1.45 (s, 9H); $\delta_C$ (75.5 MHz, $CDCl_3$): 155.6 (q), 151.3 (q), 150.6 (q), 134.4, 124.3, 107.5, 106.2, 80.1 (q), 57.4, 41.3, 29.6, 28.3 (3 × C), 27.4, 21.1, 13.5.; *m/z*: 371 [M$^+$($^{81}$Br), 1%], 369 [M$^+$($^{79}$Br), 1%], 270 [M$^+$($^{81}$Br)–(Boc), 6%], 268 [M$^+$($^{79}$Br)–(Boc), 3%], 161 [($C_6H_8{}^{81}$Br), 22%], 159 [($C_6H_8{}^{79}$Br), 21%], 81, 79; EA. ($C_{17}H_{24}BrNO_3$), Calculated (Found)%: 55.14 (55.29)% C, 6.53 (6.24)% H, 3.78 (3.80)% N.

*Cycloaddition reactions for* (**10a–c**)

The furans (**9a–c**) (5 mmol) was heated up to 110°C in 10 ml of toluene for 4 days at which time the reaction mixture was cooled and concentrated. Purification by column chromatography afforded the cycloadducts, and in all cases, the polarity of the cycloadduct was greater that its precursor.

*tert-Butyl 7b-bromo-5,5a,6,7,7a,7b-hexahydro-2a,5-epoxycyclopenta[cd]isoindole-1-carboxylate* (**10a**): White solid, (0.77 g, 45%); m.p. 77–79°C; TLC, (hexane: EtOAc (7:3)): $R_f$ 0.40; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 2980 (s, C–H), 2930 (s, C–H), 1716 (s, C=O), 1148 (s, C–O), 612 (m, C–Br). $\delta_H$ (300 MHz, $CDCl_3$): 6.59–6.50 (m, 2H), 4.84 (d, 1H, *J* = 1.5 Hz), 4.40 (t, 1H, *J* = 8.0 Hz), 4.06–3.88 (m, 2H), 2.30–2.16 (m, 1H), 1.93–1.85 (m, 2H), 1.66–1.58 (m, 1H), 1.45 (s, 9H); $\delta_C$ (75.5 MHz, $CDCl_3$): 155.2 (q), 143.2,142.0, 95.4 (q), 80.3 (q), 79.7, 70.3 (q), 62.4,51.0, 49.2, 28.7 (3 × C), 25.4, 20.1; *m/z*: 343 [M$^+$($^{81}$Br), 1%], 341 [M$^+$($^{79}$Br), 1%], 286 [M$^+$($^{81}$Br)–($^t$Bu), 30%], 284 [M$^+$($^{79}$Br)–($^t$Bu), 29%], 205 [M$^+$($^{81}$Br)–($^t$Bu + $^{81}$Br), 85%], 139 [M$^+$($^{81}$Br)–($^t$Bu + $C_5H_6{}^{81}$Br), 100%], 81, 57. EA. ($C_{15}H_{20}BrNO_3$), Calculated (Found)%: 52.64 (52.65)% C, 5.89 (5.66)% H, 4.09 (4.15)% N.

*tert-Butyl 8b-bromo-5a,6,7,8,8a,8b-hexahydro-5H-2a,5-epoxycyclobenzo[cd]isoindole-1-carboxylate* (**10b**): Yellow solid, (0.26 g, 15%); m.p. 82–84°C; TLC, (hexane: EtOAc (4:1)): $R_f$ 0.18; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 2953 (s, C–H), 2924 (s, C–H), 1702 (s, C=O), 1169 (s, C–O), 709 (m, C–Br); $\delta_H$ (300 MHz, $CDCl_3$): 6.44 (dd, 1H, *J* = 1.8 Hz, *J* = 5.7, AB), 6.37 (d, 1H, *J* = 5.7 Hz, AB), 4.80 (d, 1H, *J* = 1.8 Hz, AB), 4.64 (s, 1H), 4.28 (d, 1H, *J* = 12.5 Hz, AB), 3.52 (d, 1H, *J* = 12.5 Hz, AB), 2.31–1.40 (m, 7H), 1.19 (s, 9H); $\delta_C$ (75.5 MHz, $CDCl_3$): 158.2 (q), 135.4, 134.7, 92.2 (q), 80.3 (q), 75.6, 70.1 (q), 54.2, 49.2,43.6, 28.4 (3 × C), 25.7, 21.5, 21.0; *m/z*: 357 [M$^+$($^{81}$Br), 3%], 355 [M$^+$($^{79}$Br), 3%], 256 [M$^+$($^{81}$Br)–(Boc), 11%], 254 [M$^+$($^{79}$Br)–(Boc), 3%], 241 [M$^+$($^{81}$Br)–(Boc + $CH_3$), 6%], 161 [($C_6H_8{}^{81}$Br), 25%], 159 [($C_6H_8{}^{79}$Br), 6%]; EA. ($C_{16}H_{22}BrNO_3$), Calculated (Found)%: 53.94 (53.90)% C, 6.22 (6.27)% H, 3.93 (3.92)% N.

*tert-Butyl 8b-bromo-5-methyl-5a,6,7,8,8a,8b-hexahydro-5H-2a,5-epoxycyclobenzo[cd]isoindole-1-carboxylate* (**10c**): As yellow solid, (0.31 g, 17%); m.p. 85–87°C; TLC, (hexane: EtOAc (4:1)): $R_f$ 0.16; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 2982 (s, C–H), 2942 (s, C–H), 1716 (s, C=O), 1168 (s, C–O), 614 (m, C–Br); $\delta_H$ (300 MHz, $CDCl_3$): 6.32 (d, 1H, *J* = 5.2 Hz, AB), 6.31 (d, 1H, *J* = 5.2 Hz, AB), 4.64 (s, 1H), 4.25 (d, 1H, *J* = 12.4 Hz, AB), 3.66 (d, 1H, *J* = 12.4 Hz, AB), 2.31 (s, 3H), 2.26–1.45 (m, 7H), 1.32 (s, 9H); $\delta_C$ (75.5 MHz, $CDCl_3$): 151.5 (q), 132.2,131.8, 89.8 (q), 85.0 (q), 80.3 (q), 69.4 (q), 55.8, 52.9, 49.5, 28.4 (3 × C), 24.2, 21.0, 20.6, 17.5; *m/z*: 371 [M$^+$($^{81}$Br), 5%], 369 [M$^+$($^{79}$Br), 5%], 314 [M$^+$($^{81}$Br)–($^t$Bu), 6%], 270 [M$^+$($^{81}$Br)–(Boc), 95%], 268 [M$^+$($^{79}$Br)–(Boc), 96%],161 [($C_6H_8{}^{81}$Br), 11%], 159 [($C_6H_8{}^{79}$Br), 11%]; EA. ($C_{17}H_{24}BrNO_3$), Calculated (Found)%: 55.14 (55.19)% C, 6.53 (6.43)% H, 3.78 (3.92)% N.

*Synthesis of* (**13a–b**)

To a solution of and bromo-oxa and thio heterotricycles (**12a–b**) [synthesised as in ref. 2d] (0.80 mmol) in dry DCM (5 ml) cooled to –78°C under $N_2$ was added $BF_3{\cdot}Et_2O$ (0.11 ml, tech 50%, 0.88 mmol) in DCM (5 ml) over 3 min. After being stirred at same temperature for 15 min, the reaction mixture was warmed to 0°C over period of 3 h. The cooling bath was removed and the reaction mixture was stirred at room temperature for another 4 h. The reaction mixture was then diluted with water (5 ml) and the layers were separated. The aqueous layer was further extracted with DCM (10 ml) and the combined organic layers were washed with water (2 × 4 ml), dried (anhydrous $MgSO_4$) and concentrated in *vacuo*. The residue was subjected to flash column chromatography to afford following compounds.

*1,3-dihydro-2-benzofuran-5-ol* (**13a**): White solid, (0.08 g, 76%); m.p. 67–69°C, TLC, (hexane: EtOAc (6:2)): $R_f$ 0.38; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 3226 (s, O–H), 2929 (s, C–H), 2867 (s, C–H), 1030 (s, C–O); $\delta_H$ (300 MHz, $CDCl_3$): 7.08 (d, 1H, *J* = 8.1 Hz, AB), 6.74 (d, 1H, *J* = 8.1 Hz, AB), 6.71 (s, 1H), 5.06 (s, 4H), 3.61 (s, OH); $\delta_C$ (125 MHz, $CDCl_3$): 155.4 (q), 140.9 (q), 130.9 (q), 121.8, 114.6, 106.4, 73.4, 73.2; *m/z* (GC–MS): 135 [M$^+$–(H), 34%], 119 [M$^+$–(OH), 13%], 75[$C_6H_3$, 22%]; EA. ($C_8H_8O_2$), Calculated (Found)%: 70.57 (70.69)% C, 5.92 (6.14)% H.

*1,3-dihydro-2-benzothiophene-5-ol* (**13b**): Yellow solid, (0,09 g, 72%); m.p. 62–64°C TLC, (hexane: EtOAc (6:2)): $R_f$ 0.43; $\upsilon_{max}$ (thin film)/cm$^{-1}$: 3365 (s, O–H), 2920 (s, C–H), 2851 (s, C–H), 1100 (s, C–O), 1026 (s, C–S); $\delta_H$ (300 MHz, $CDCl_3$): 6.90 (d, 1H, *J* = 8.4 Hz, AB), 6.72 (d, 1H, *J* = 8.4 Hz, AB), 6.51 (s, 1H), 4,97 (s, 4H), 4,25 (s, OH); $\delta_C$ (125 MHz, $CDCl_3$): 154.2 (q), 138.2 (q), 131,0 (q), 122.6, 115.0, 104.3, 73.4, 73.3; *m/z* (GC–MS): 151 [M$^+$–(H), 46%], 135 [M$^+$–(OH), 8%], 75[$C_6H_3$, 20%]; EA. ($C_8H_8OS$), Calculated (Found)%: 63.13 (63.31)% C, 5.30 (5.22)% H.

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